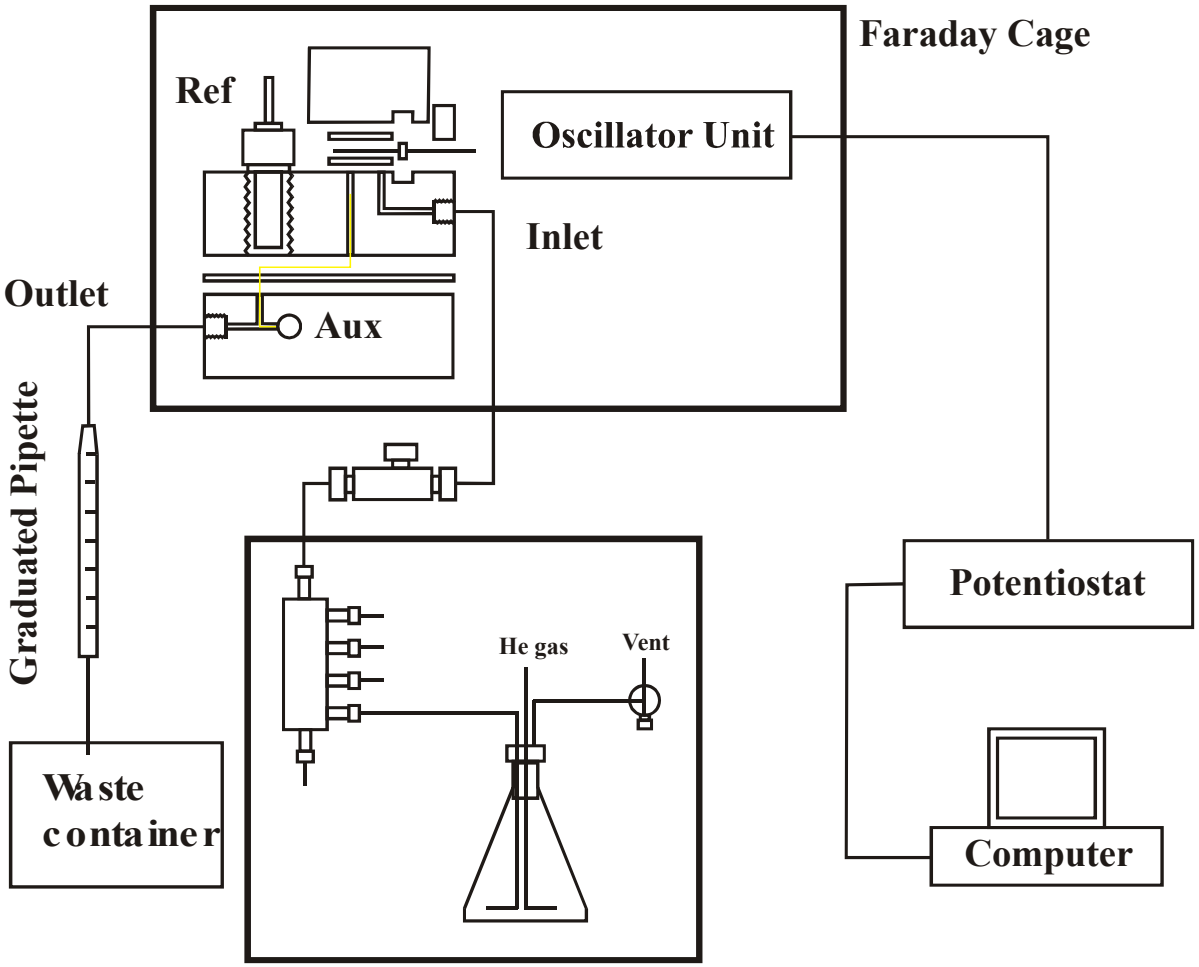
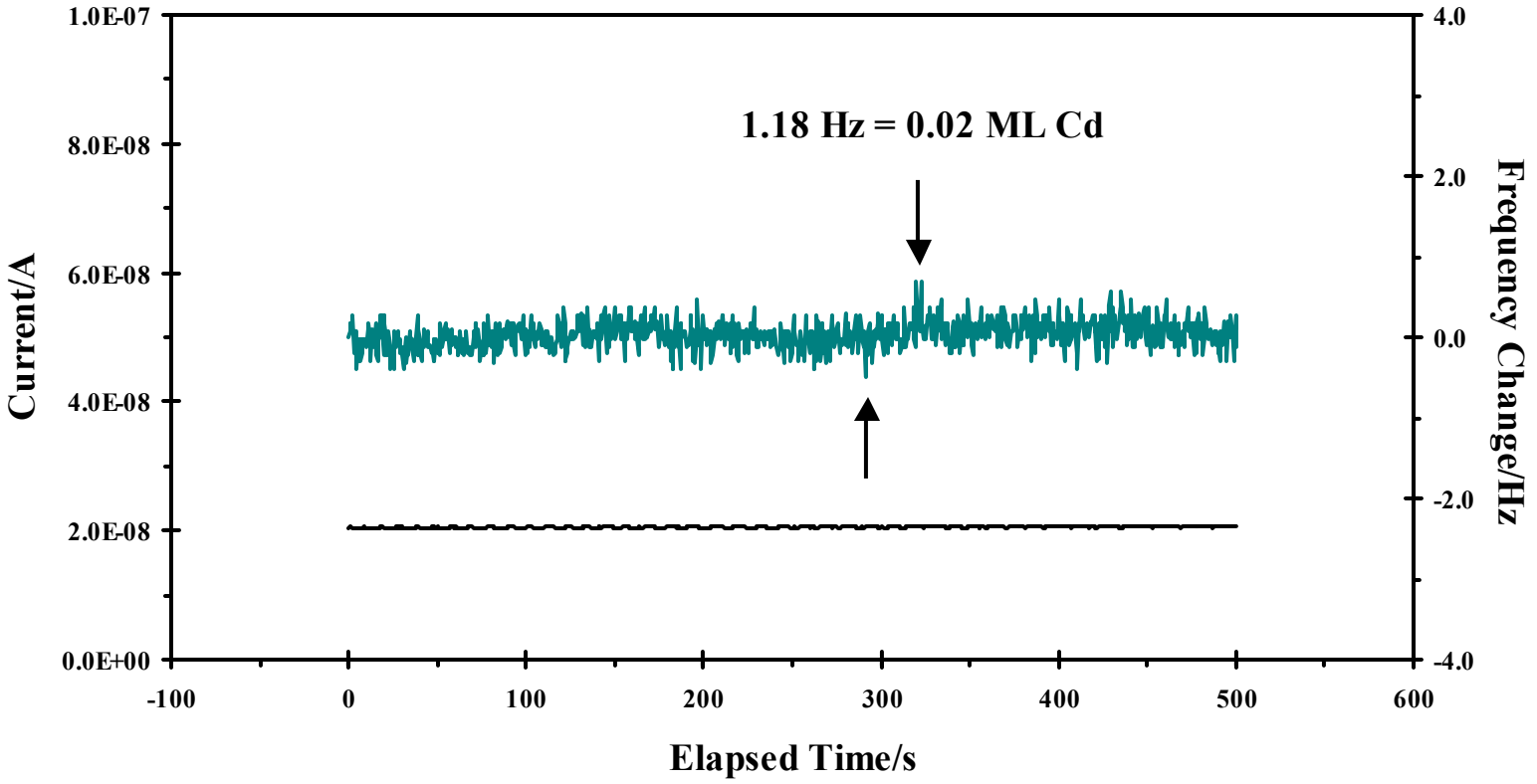
NSF DMR-0075868: Surface Chemistry Studies During Thin-Film Growth Using Electrochemical Atomic Layer Epitaxy. Professor Stickney's group is ethnically and culturally diverse as can be seen in the attached picture. All students have received some support from the NSF. From left to right: Marcus Lay (Brooklyn, New York), Lindell Ward (Missouri), John Stickney (Berkeley, California), Billy Flowers (Alabama), Nattapong Srisook (Thailand), Ken Mathe (Kroonstad, South Africa), Madhivanan Muthuvel (Madras, India), Raman Vaidyanathan (Madras, India).

EQCM with a Thin Layer Flow Cell



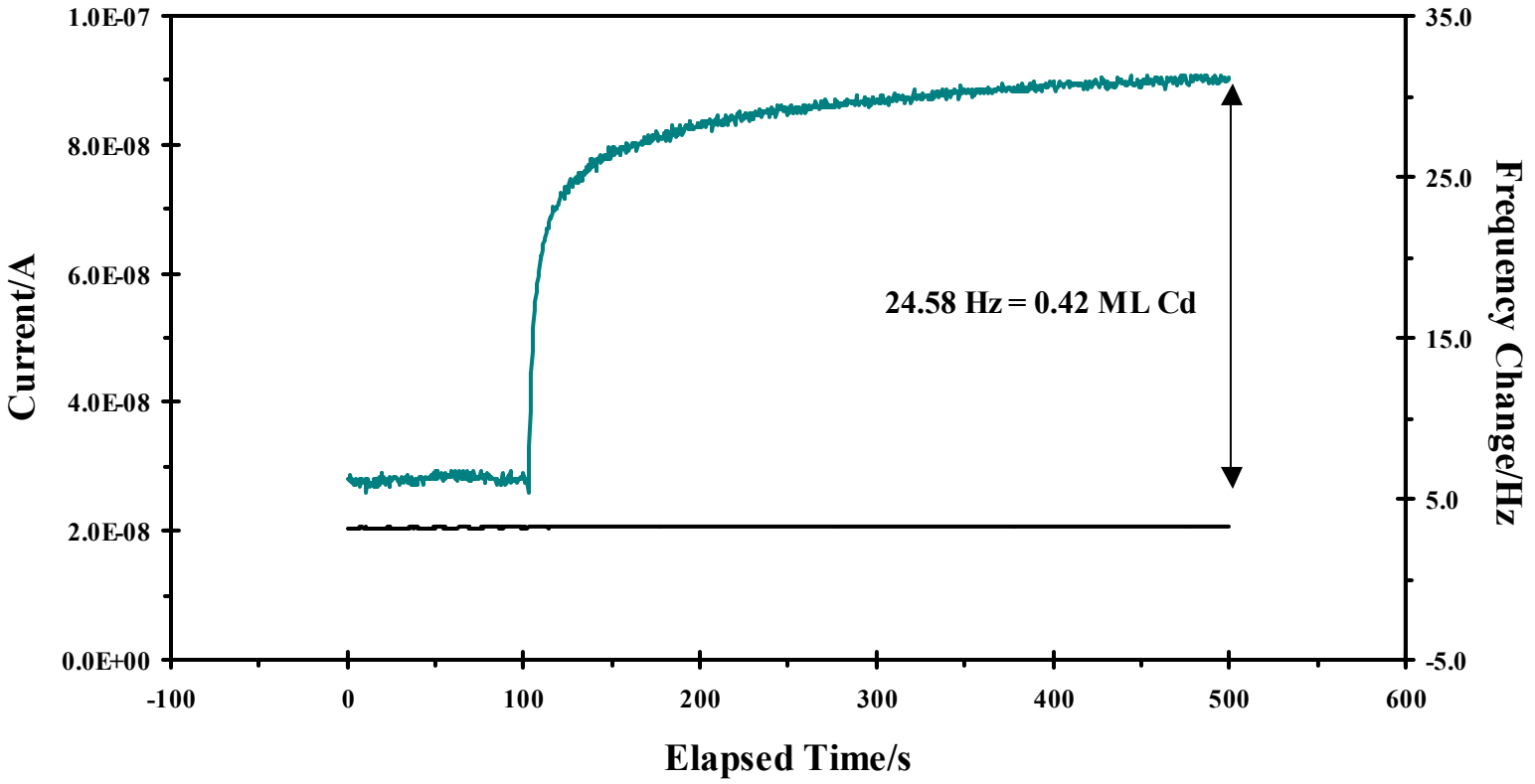
NSF DMR-0075868: Surface Chemistry Studies During Thin-Film Growth Using Electrochemical Atomic Layer Epitaxy. In an effort to better follow the growth of thin films during there deposition using atomic layer epitaxy, we have built a electrochemical quartz crystal microbalance system that uses a flow cell. In this way, the mass of the deposits can be followed, as well as the charges for each atomic layer step in the deposition. Solutions are pumped using pressurized He, and a Teflon valve selects which solution is delivered to the cell.

0.1 M $HClO_4$, Flow Rate = 0.060 mL/min with Helium pressure.



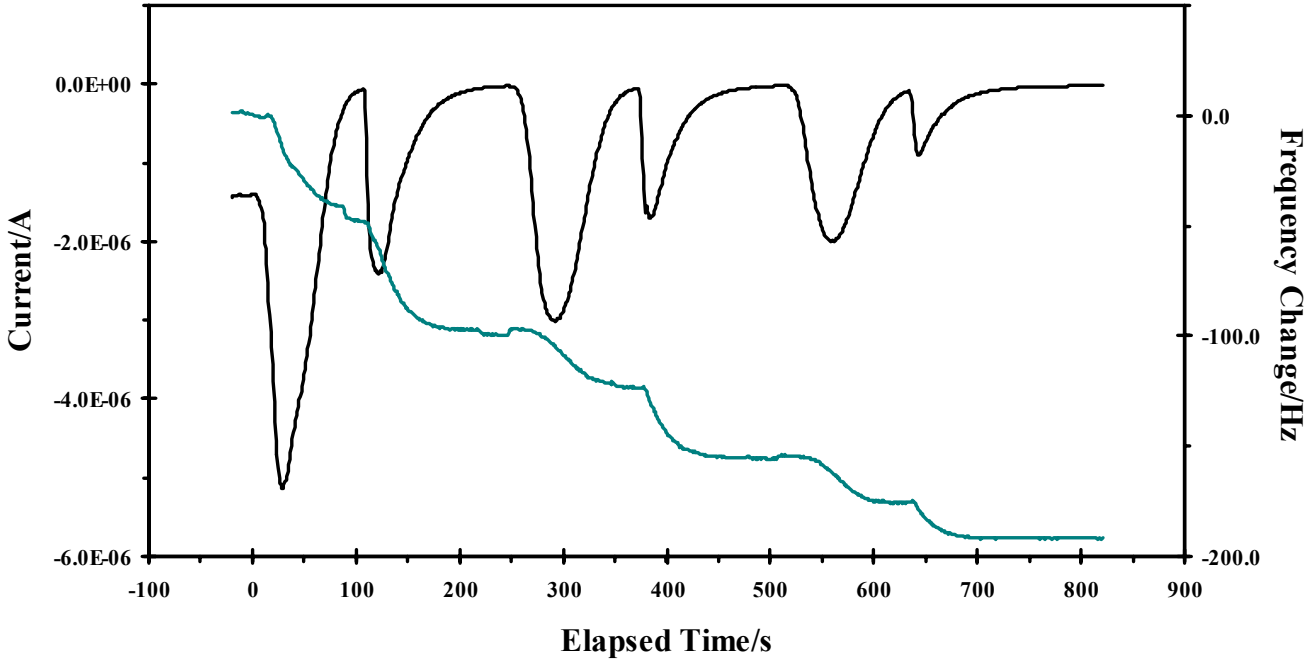
The noise level for the EQCM is about 2% of a monolayer of Cd atoms with the solutions flowing. This is essentially the same as when the solutions are not flowing. This matches well with the uncertainty in the charge measurements. Thus the flexibility of using a flow cell has been achieved without any loss of sensitivity.

0.1 M $HClO_4$, Flow Rate = 0.428 mL/min with Helium pressure.



Standard procedures are to stop flowing during deposition. However, as this graph shows, there is a large, slow change in mass when flow is stopped. This probably has to do with forces on the crystal during flow. The crystal is held in between two rubber gaskets. When flow is stopped, the forces change on the crystal, and it takes considerable time for the system to equilibrate. The solution has been to continuously pump solutions, simply switching which is being sent to the cell. There is no problem when the system is run in this mode.

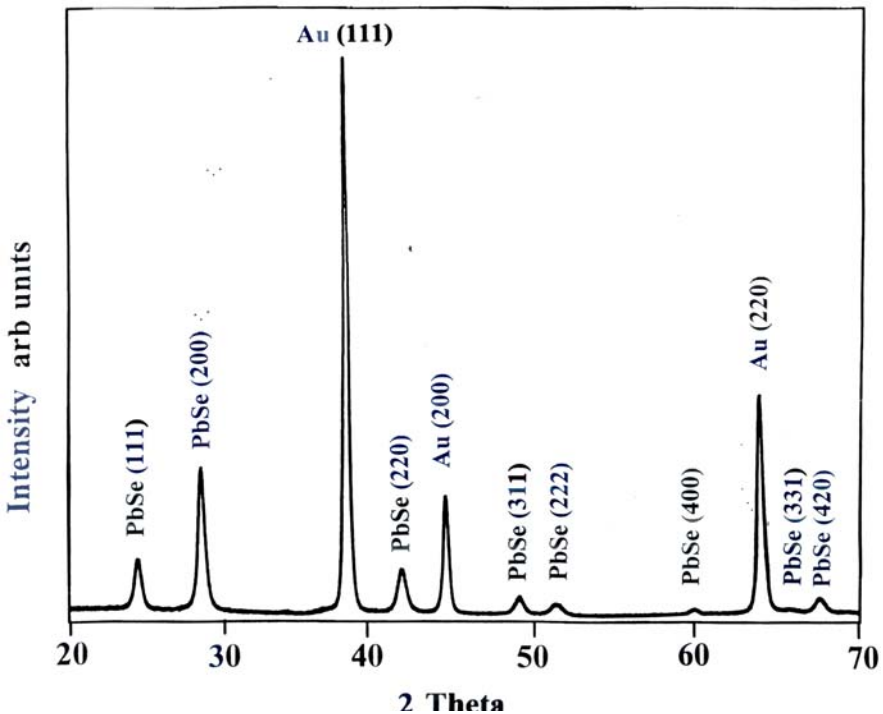
Three Cycles of CdSe
Se Deposition Time = 30 s.

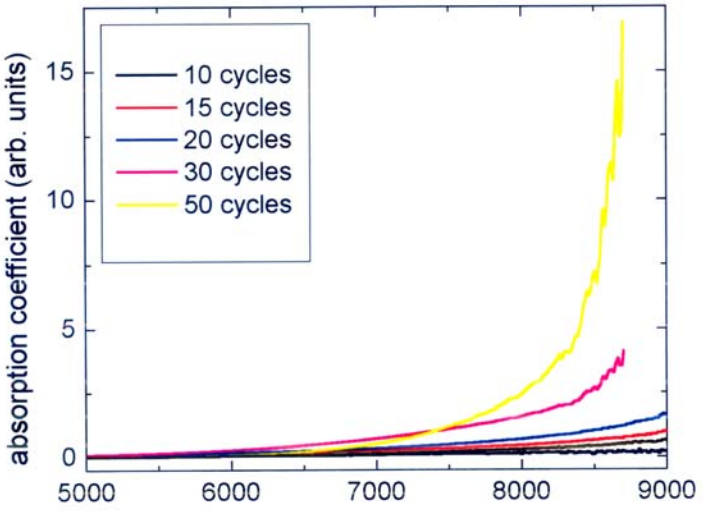


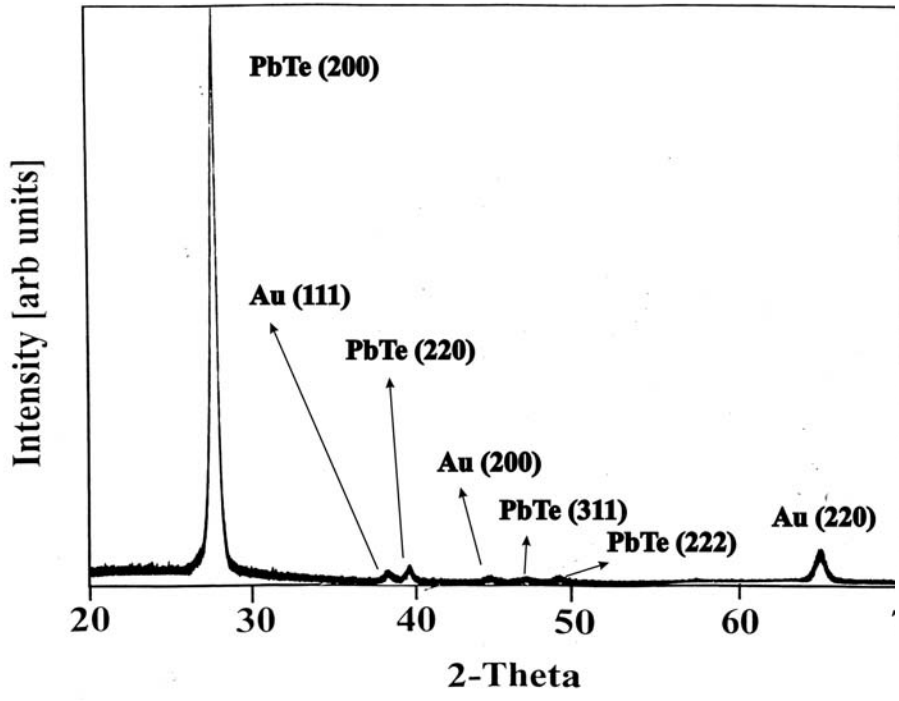
Coverage	Cycle # 1		Cycle # 2		Cycle # 3	
	Se	Cd	Se	Cd	Se	Cd
Coulometry	1.086	0.815	0.712	0.503	0.487	0.250
Gravimetry	1.059	0.783	0.582	0.493	0.452	0.249

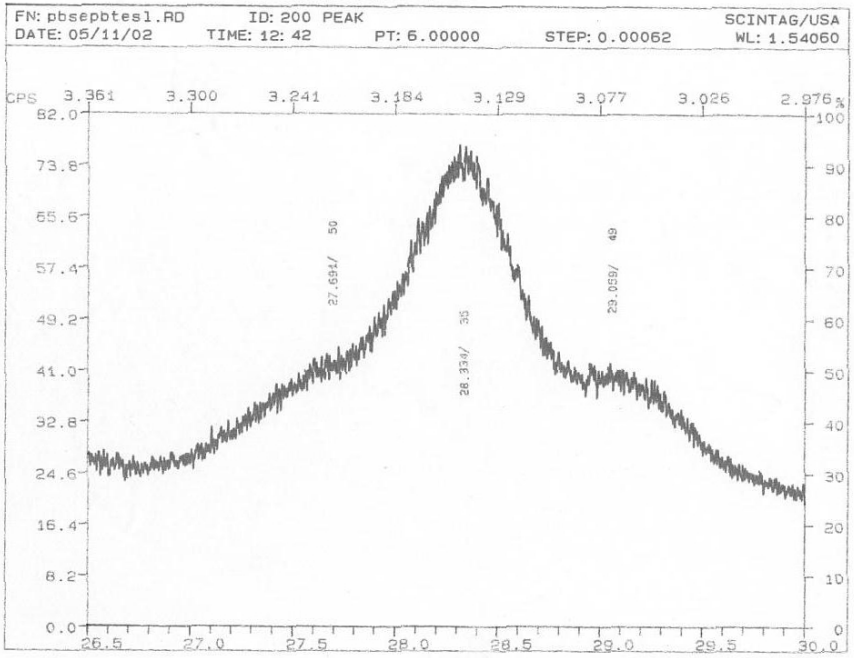
The attached diagram is for the first three cycles of deposition and shows both charges and mass changes. The first cycle has more deposition then subsequent. There are a couple of reasons for this. One is that a too negative value for Se deposition has been used. This is easily fixed. The second reason is that the potentials needed to deposit the atomic layers shift as the deposit grows. This has to do with the formation of a semiconductor on a metal surface. The semiconductor develops a space charge layer, and this decreases the potential actually applied at the surface of the deposit. The solution is simply to shift the potential a small amount for the first 30 or so cycles, which is easy to do with the deposition program.

Confinement of PbSe Thin Films









We have just begun to deposit IV-VI compounds. They are used for IR detectors. They have very large Bohr radii for excitons, and thus show quantum confinement effects readily. The first compound we tried was PbSe, the upper left figure is an XRD pattern of PbSe. It shows a high quality poly-crystalline deposit. The top right is a series of reflection spectra for deposits formed with different numbers of cycles. The band gap changes by over a volt for the different deposit thicknesses, due to quantum confinement. Next we tried PbTe, and instead of a poly crystalline deposit, we observed a single peak in the XRD, suggesting a very good lattice match with the Au, and a single crystalline deposit. This is the best quality electrodeposited compound semiconductor, with out annealing, that we have observed in the literature, besides the oxides. We are very excited about the result. We have thus begun to look at superlattices formed using PbSe and PbTe. Our first deposit has shown satellite peaks characteristic of the period used to form the deposit. This is very encouraging, and is being pursued presently.